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NATURAL RUBBER LOADED WITH LOCAL MATERIALS. III. CREEP PROPERTIES

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The creep properties (creep rate, creep modulus, creep compliance and tensile creep) of natural rubber loaded separately with local clay, limestone, silica-sand and charcoal have been examined as a function of filler loading, filler particle size, stress level and temperature. Results reveal that creep rate increases with increasing loading, stress level and temperature. The clay loaded composites show lower creep rate and energy to resist deformation than for composites loaded with limestone, silica sand and charcoal. Clay therefore shows a clear advantage over limestone, silica-sand and charcoal in creep deformation resistance when used as fillers in natural rubber.

Key words: Creep properties, Local materials, Natural rubber composite, Filler loading, Stress level, Temperature.

Introduction

In many applications, materials are required to sustain steady loads for long periods of time. For example, in the blades of a turbine rotor, plastic mountings for parts of electrical devices, timber beams in the roof of a building, filaments in vacuum tubes, steel cables and concrete in a prestressed concrete beam and lead sheaths on telephone cables (Richards 1961). Under such conditions the material may continue to deform until its usefulness is seriously impaired. Such time-dependent deformations may be almost imperceptible, but over the lifetime of a structure they can grow large and even result in final fracture without any increase in load. If under any conditions, deformation continues when the load is held constant, this additional deformation is known as creep.

In our effort to characterize natural rubber loaded with local clay, limestone, charcoal and silica sand, we have determined the cure, mechanical and electrical properties of natural rubber loaded with these local materials. Results revealed that clay is the best of these materials for scorch enhancement tensile strength reinforcement and electrical conductivity.

In the present work, creep, an important engineering material property which measures the rate of deformation of a material has been determined for composites loaded with the local materials under examination. The creep rate, tensile creep, creep modulus and creep compliance of the loaded composites have been determined as a function of filler loading, filler particle size, stress level and temperature.

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Experimental

Materials. Forty-one (41) conventional accelerator/sulphur compounds were tested as indicated in Tables 1 and 2. The natural rubber used was a Nigerian Standard Rubber Grade 10 (NSR10) produced at the Michelin Plantations, Araromi-Obu, Ondo State, Nigeria. Clay was collected from Afao-Ekiti, Ekiti State, Nigeria; Limestone was collected from Arimogija, Ondo State, Nigeria; silica sand was collected from Igbokoda, Ondo State; Nigeria, whilst wood charcoal was purchased at the Erekesan market, Akure, Ondo State, Nigeria.

Mixing. Mixing was done in accordance with the procedure described by International Standard Organisation . The water cooled 6 laboratory two roll mill was carefully controlled and made to attain a maximum temperature of 70°C and maximum speed of 24 rpm.

Curing was carried out as described by the British Standard Organisation . Moulding of dumbell test pieces for mechanical properties determination and the disk for resilience determination was done as described by the International Standard Organisation and British equivalent. The tensile strength, modulus and elongation at break were determined using Instron Universal testing machine, model 4301 in accordance with International Standard Organisation.

Mineral analysis. Mineral analysis for clay, limestone, silica sand and charcoal samples were carried out making use of colorimetric method for alumina, silica sulphur and AAS for the rest major elements. Calorific method was used for carbon determination (Table 3).

Creep measurement. Milling compounding and curing of composites were done as described in BSO 1971. The dumbell

Table 1
Formulation of composites examined

Composites	Parts per hundred rubber (pph)
Natural rubber	100
Zinc oxide	5
Stearic acid	3
MBT(a)	1
Sulphur	3
Filler	Variable

(a) Mercaptobenzothiazole

shaped samples were tested for creep using a tensiometer. The test piece was hung to the upper part of the lower end of the test piece whilst the scale plan bearing the load was hung to the hook. A costant load of $10km^{-2}$ was then put in the scale pan and the extension produced by the load was read as a function of time for 24 hours at 29°C (BSO 1969; Adu 1991).

The experiments were repeated as (20 and 30) KNm^{-2} using constant temperature at 29 °C. The experiments were also repeated at 50 and 67 °C . The temperature was kept constant within ± 2 °C.

Data analysis. From the data on elongation and time, the strain was evaluated and plotted against time. The creep behaviour was obtained from the secondary stage strain rate. The logarithm of creep rate was plotted against inverse absolute temperature and the activation energy of creep evaluated (equation 1). The logarithm of creep rate was plotted against logarithm of stress and the constants β and evaluated (equation 2)

$$\text{Log } \varepsilon' = \log A - \frac{\Delta Ea}{RT} \quad \ldots\ldots(1)$$

$$\text{Log } \varepsilon' = \log \beta + n \log \sigma \quad \ldots\ldots(2)$$

where ε' = creep rate, σ = stress, ΔEa = activation energy of creep, A, β and n are constants (Parker 1957; Edward 1958; Richard 1961; Ashby and Jones 1980; Schackelford 1990).

Results & Discussion

The plots of strain versus time for clay, limestone, silica sand and charcoal loaded vulcanizates are similar (Fig 1). The creep rate, creep modulus, creep compliance and the tensile creep evaluated from these plots ; (British Standard Organisation 1958; Bueche 1961) are (Shackleford 1990) presented in Table 4 for clay and limestone. A typical plot of these parameters against filler loading is shown in Fig 2. It is observed

Table 2
Formulation composite as a function of filler loading and particle size

Composite	Filler loading (pph)	Filler particle size (μm)
(standard) N	-	-
NC1	12	300
NC2		"
NC3	36	"
NC4	48	"
NC5	72	"
NC6	28	45
NC7	28	75
NC8	28	150
NC9	28	300
NC10	28	850
NCC1	12	300
NCC2	28	"
NCC3	36	"
NCC4	48	"
NCC5	72	"
NL1	12	"
NL2	28	"
NL3	36	"
NL4	48	"
NL5	72	"
NL6	28	45
NL7	28	75
NL8	28	150
NL9	28	300
NL10	28	850
NCL1	12	300
NCL2	28	"
NCL3	36	"
NCL4	48	"
NCL5	72	"
NCH1	12	300
NCH2	28	"
NCH3	36	"
NCH4	48	"
NCH5	72	300
NS1	12	
NS2	28	
NS3	36	
NS4	48	
NS5	72	

N		Gum compound without filler (Standard)
NC	-	Clay loaded composite
NCC	-	Calcined clay loaded composite
NL	-	Limestone loaded composite
NCL	-	Calcined limestone loaded composite
NCH	-	Charcoal loaded composite
NS	-	Silica sand loaded composite

Table 3
Chemical composition of the materials used in the work

	S_iO_2	SO_2	Al_2O	K_2O	Na_2O	CaO	MgO	Fe_2O_3	CO_2	Left over
Clay	48.83	23.81	10.09	5.91	0.59	1.34	1.02	4.91	Nd	3.50
Limestone	4.26	1.49	1.16	6.21	0.70	52.92	10.36	4.02	Nd	18.88
Silica sand	78.13	2.80	1.06	0.24	0.18	0.34	0.02	2.09	Nd	15.14
Charcoal	22.44	2.40	0.17	0.31	0.29	0.22	0.09	0.07	51.72	22.29

nd, not determined

Table 4
Creep properties of uncalcined fillers as a function of loading and temperature

		302K (3.31 x 10^3K^{-1})				323K (3.10 x 10^3K^{-1})				340K (2.9 x 10^3)K^{-1}			
Filler	Filler Content (pph)	Creep Rate	Creep Modulus	Creep Compliance	Tensile Creep	Creep Rate	Creep Modulus	Creep Compliance	Tensile Creep	Creep Rate	Creep Modulus	Creep Compliance	Tensile Creep
Nil	ZERO	.022	.142	-.142	1.875	.028	.162	-.162	-.162	1.600	.036	.246	1.857
Clay	12	.019	.104	-.104	1.209	.023	.108	-.108	1.259	.027	.112	-.112	1.225
"	28	.019	.162	-.162	1.217	.021	.112	-.112	1.222	0.27	.166	-.166	1.225
"	36	.081	.156	-.156	1.079	.102	.156	-.156	1.313	R	.356	-.356	1.463
"	48	.020	.264	-.264	1.223	.028	.268	-.268	1.400	.036	.365	-.365	1.382
"	72	.303	.102	-.102	1.563	.047	.162	-.162	-1.625	.066	.365	-.365	2.091
Lime stone	12	.018	.048	-.048	1.185	.028	.156	-.156	1.267	.039	.162	-.162	1.117
	28	.020	.054	-.054	1.135	.026	.102	-1.02	1.214	.039	.258	-.258	1.209
"	36	.074	.054	-.054	1.282	.100	.102	-.102	1.286	.141	.204	-.204	1.284
"	48	.024	.108	-.108	1.500	.029	.108	-.108	1.318	.039	.598	-.599	.667
"	72	.028	.234	-.234	1.357	.033	.234	-.239	1.429	.048	.317	-.317	1.571

that creep rate of the loaded vulcanizates follows the increasing trend: clay limestone < charcoal < silica sand. This trend indicates that the rate of deformation follows the reverse trend. Clay and limestone loaded vulcanizates show better resistance to deformation than charcoal and silica sand. Creep rate increases with increasing filler loading. The effects of filler particle size on creep rate shows an initial increase before a progressive decrease with increasing particle size (Fig 3). The calcined clay loaded composites show higher creep rate than the composites loaded with uncalcined clay. The same trend is observed for calcined and uncalcined limestone loaded composites.

Charcoal shows exceptionally enhanced creep modulus followed in a decreasing order by silica sand, clay and limestone. Creep modulus increases with increasing filler loading. Similar behaviour has been observed for particulate fillers . Creep modulus shows an initial increase before a progressive decrease with increasing filler particle size (Fig 3). The calcined fillers show superior creep modulus compared to the corresponding uncalcined fillers.

The creep compliance follows the reverse trend of modulus. This is not surprising as creep compliance is the reciprocal of creep modulus. Creep compliance follows the decreasing trend limestone > clay > silica sand > charcoal. This

Table 5

Activation parameters of creep deformation of the composites examined as a function of filler loading at 300μm particle size

Filler	Filler loading (pph)	Arrhenius constant	Activation energy (ΔEa) J mol^{-1}	Average activation energy J mol^{-1}
Nil	Nil	1.61	2.75	2.75
Clay	12	1.43	2.47	
	28	1.42	2.73	
	36	2.19	2.88	2.76
	48	1.54	2.86	
	72	1.86	2.88	
Limestone	12	1.62	3.16	
"	28	1.59	2.75	
"	36	2.16	2.83	3.06
"	48	1.57	3.25	
"	72	1.54	3.33	
Charcoal	12	1.82	4.16	4.86
"	28	1.82	5.58	
"	36	R	R	
'	48	R	R	
	72	R	R	
Silica sand	12	1.62	2.08	
	28	1.58	2.50	
	36	1.66	2.75	3.23
	48	1.98	5.58	
	72	R	R	

property decreases with increasing filler loading but decreases to a minimum and thereafter increase with increasing filler particle size.

Table 4 presents the tensile creep of the composites as a function of filler loading. It is observed that tensile creep is comparable for all fillers. This property generally increases with increasing filler loading but increases reaches a maximum and thereafter decreases with increasing filler particle size. The calcined fillers show comparable tensile creep to the corresponding uncalcined fillers.

The creep rate is observed to increase with increasing temperature. This trend has been observed for some other materials (Haydeen *et al* 1965). The plots of logarithm of creep rate versus inverse absolute temperature show straight line (Fig 4) similar to those reported by Shackelford (1990) and Richards (1961). The slopes and intercepts of the plots were evaluated using least square method. Table 5 presents the values of the parameters evaluated. It is observed that the activation energy required to resist deformation by clay composite is lower than the activation energy required to resist deformation by the composites loaded with limestone, silica sand and charcoal. This observation is an advantage for clay whose creep rate has been observed to be lower than that of silica sand and charcoal.

The variation of creep rate as a function of stress level is presented in Table 6. It is observed that the charcoal and silica sand loaded vulcanizates at relatively high loading ruptured

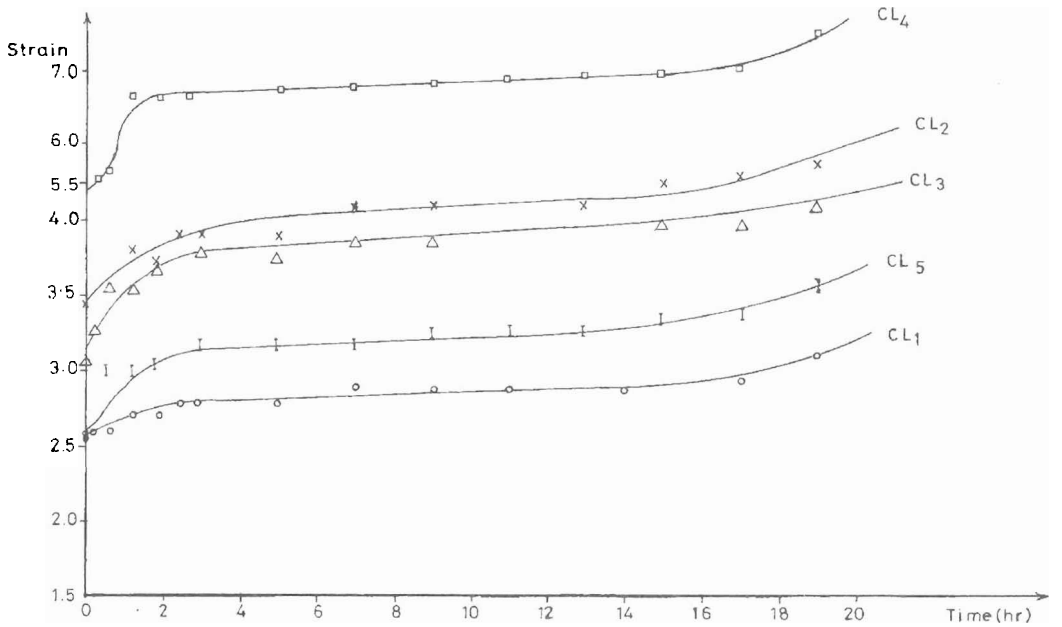

Fig 1. Plots of strain versus time for the clay-filled vulcanizates.

Table 6

Creep properties as a function of stress level for uncalcined fillers

Filler	Filler Content (pph)	At10K Nm^2 Creep rate h^{-1}	Creep modulus	Creep compliance	Tensile creep	At 20K Nm^2 Creep rate h^{-1}	Creep modulus	Creep compliance	Tensile creep	A 30K Nm^2 Creep rate h^{-1}	Creep modulus	Creep compliance	Tensile creep
Unfilled	Zero	.021	.146	-.146	1.857	.044	.162	-.162	1.227	.063	.168	-.168	1.216
Clay	28	.028	.156	-.156	1.225	.055	.311	-.311	1.135	.078	.527	-.527	1.135
Limestone	28	.036	.258	-.258	1.269	.063	.461	-.461	1.171	.110	.778	-.778	1.080
Charcoal	28	.028	.102	-.102	1.250	.065	.157	-.157	1.222	.064	.725	-.725	1.224
Silica sand	28	.029	.258	-.258	1.229	.058	.421	-.421	1.212	R	.461	-.461	R

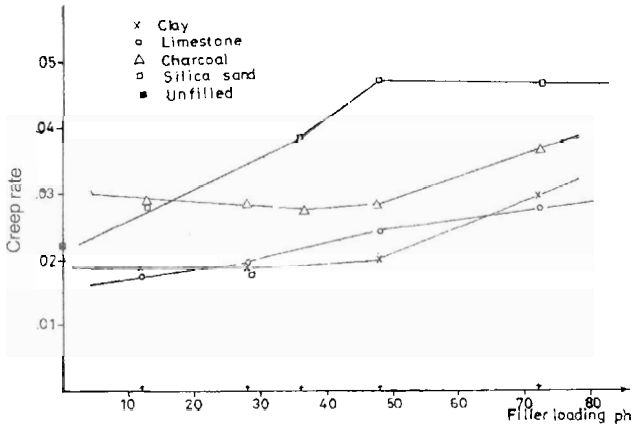

Fig 2. Plot of creep rate versus filler loading at 302K.

Table 7

Constants of the linear equation correlating creep rate and stress level.

Filler	Loading (pph)	β	n
Charcoal	28	1.58	0.42
Limestone	28	1.54	0.44
Silica sand	28	1.46	0.56
Clay	28	1.44	0.50
Nil (standard)	-	1.30	0.60

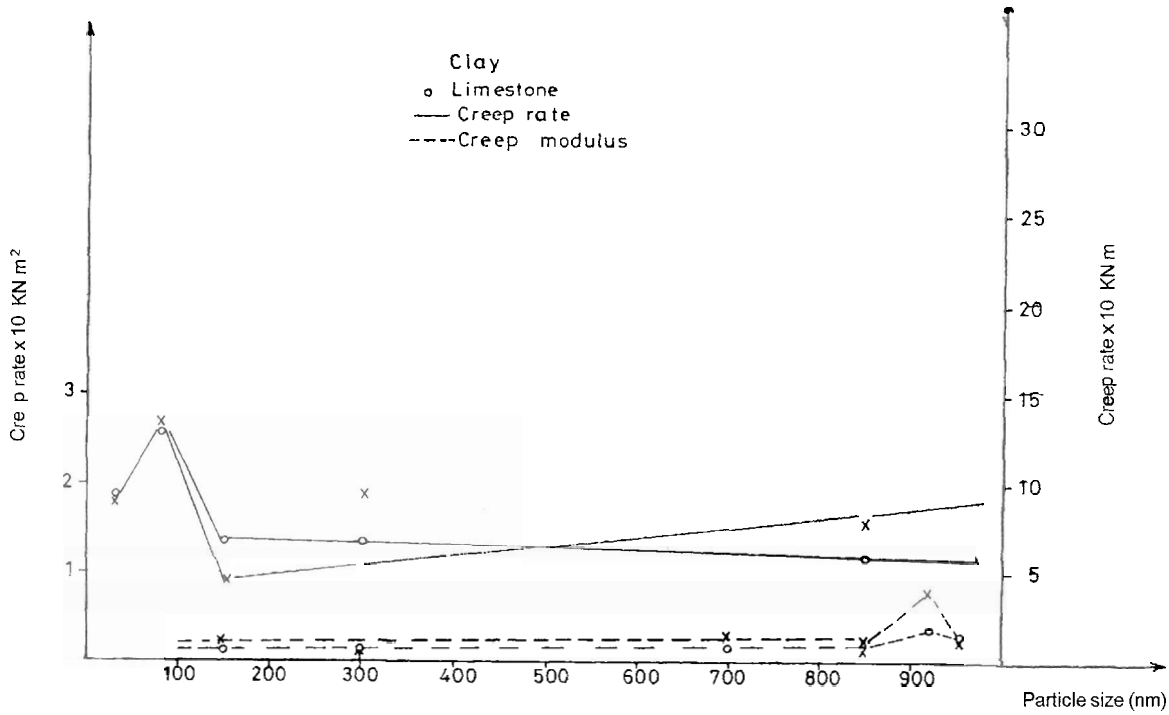

Fig 3. Plots of creep rate and modulus versus filler particle size for clay and limestone

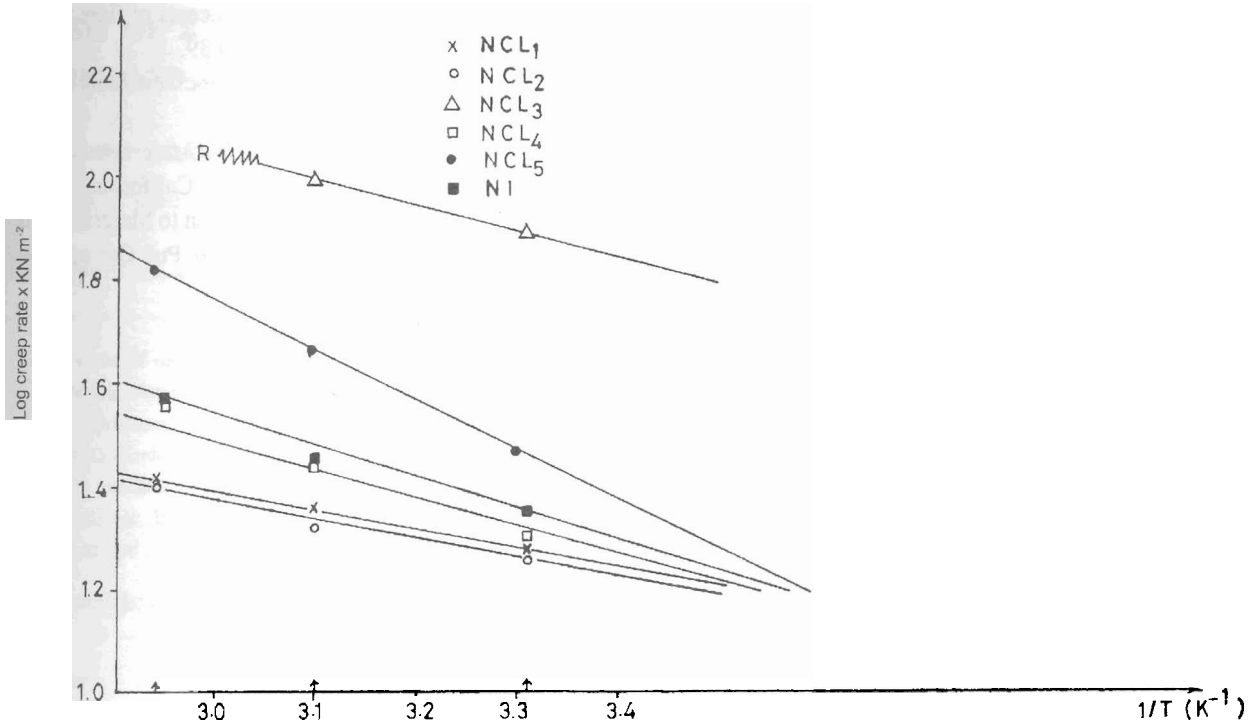

Fig 4. Plots of logarithm creep rate versus inverse absolute temperature of clay filled vulcanizates.

before the expiry of the experimentation period. Creep rate increases with the increasing stress level. The creep rate (ε') and the stress level (σ) are correlated with the equation:

$$\text{Log } (\varepsilon') = \log \beta + n \log \sigma \text{(Richards 1961)}.$$

The plot of logarithm creep rate versus logarithm stress level show linearity and the values of β and n evaluated using least square method are contained in Table 7. The linear shape of the plots is similar to that reported by Randall (1957). Values of n follow the decreasing trend: silica sand, clay, limestone and charcoal while the constant β follows the reverse trend. The significance of these constants is not immediately clear but they appear to be deformation parameters such that the higher the magnitude of n and the lower the magnitude of β, the less the activation energy required to resist deformation.

Conclusion

The results of this work have shown conclusively that:
Creep rate increases with increasing filler loading, temperature and stress level.

Within the time range used in this work, charcoal and silica sand loaded vulcanizates at relatively high filler loading ruptured before the expiry of 19 hours under constant load. They are therefore inferior to limestone and clay loaded vulcanizates in deformation resistance.

The creep rate and the activation energy required to resist deformation are lower for the clay loaded vulcanizate than for limestone, silica sand and charcoal loaded vulcanizates. Clay therefore shows a clear advantage over limestone, silica sand and charcoal in creep deformation resistance.

References

Adeosun B F, Olaofe, O 2001 Electrical conductivity of natural rubber loaded with local materials. *African Journal of Pure and Applied Sciences* (in print).

Adu O E 1991 Effect of fillers on mechanical and viscoelastic properties of cured rubber, M.Sc. Thesis, Uniben, Nigeria.

Ashby, Jones 1980 *Engineering Materials – An Introduction to their properties and Applications.* Pergamon press, Inc. Elmsford NY.

British Standard Organisation 903, part A 25 1958 *Testing Procedures and Standards:* In Rubber Tech. and manufacture Ed GM Blow 2nd ed 1975.

British Standard Organisation 903, Part A 26 1969 *Testing Procedures and Standard:* In Rubber Tech. and manufacture Ed G M Blow 2nd ed 1975.

British Standard Organisation 903, Part A 2 1971 *Testing*

Procedure and Standards: In Rubber Tech. and manufacture Ed G M Blow 2nd ed 1975.

Bueche F 1960 Molecular basis for the Mullin, effect. *J Appl Polym Sci* **4** 107–114.

Bueche F 1961 Mullins effect and rubber filler interaction. J *Appl Polym Sci* **5** 271 – 281.

Edward de Mille 1958 Campbell memorial lecture, transactions. *Am Soc Metals* **50** 84.

Parkeer E R 1957 Modern concepts of flow and fracture. *Transactions Am Metals* **50** 89.

Randall 1957 Creep data. *Am Soc Test Mats Proceedings,* **57** 854-876.

Richards C W 1961 *Engineering Materials Science.* Wads Worth Pub Coy Inc Belmont, California.

Shackelford J F 1990 Introduction to Materials Science for Engineers. 2nd ed Macmillan Pub Coy pp 289-352.